An Interacting Quantum Atoms Analysis of the Metal-Metal Bond in $[\mathbf{M_2(CO)_8}]^{\mathbf{n}}$ Systems

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Abstract

The metal-metal interaction in policarbonyl metal clusters remains one of the most challenging and controversial issues in metal-organic chemistry, being at heart of a generalized understanding of chemical bonding and of specific applications of these molecules. In this work, the interacting quantum atoms (IQA) approach is used to study the metal-metal interaction in dimetal polycarbonyl dimers, analysing bridged ($Co_2(CO)_8$)), semi-bridged ($[FeCo(CO)_8]^-$) and unbridged ($Co_2(CO)_8$, $[Fe_2(CO)_8]^{2-}$) clusters. In all systems, a delocalized covalent bond is found to occur, involving the metals and the carbonyls, but the global stability of the dimers mainly originates from the coulombic attraction between the metals and the oxygens.

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Introduction

After the discovery of the first dimetal polycarbonyl $M_2(CO)_n$ molecules, $Fe_2(CO)_9$[1] and $Mn_2(CO)_{10}$,[1–3] a vivid debate started concerning the existence and the nature of direct metal-metal (MM) chemical bonds. Although chemical intuition (here conveyed by the so-called 18-electron rule) and the observed MM distances in $M_2(CO)_n$ systems would suggest the presence of single, localized MM bonds,[4] it was soon recognized that such a simplified scheme cannot correctly explain this bonding, which actually originates from the interplay of more valence bond configurations. The complexity of the interactions increases when one or more carbonyl ligands bridge two metals (*supported* MM bond), and the presence of a direct MM bond is in fact more questionable.[5] Despite the diamagnetic nature of $Fe_2(CO)_9$ and its short MM distance (2.523 Å), many theoretical studies over the years have excluded a "localized" two-center-two-electrons (2c2e) bond,[6] although this remains matter of discussion.[7] Furthermore, early experimental[8] and theoretical[9] studies on $Mn_2(CO)_{10}$ raised some doubts about the presence of a direct MM bond even in systems without bridging carbonyls (*unsupported* MM bond), justifying the stability of this compound with favorable 1,3 Mn...CO interactions.[10] In order to ascertain which force plays in fact the major role in stabilizing a cluster, accurate calculations and energy partitioning are necessary, but this was not possible at the time of those investigations.

A breakthrough occurred when the Quantum Theory of Atoms in Molecules (QTAIM)[11] could be applied to study these molecules.[12] In principle, QTAIM is an unbiased method to analyze the chemical bond between two atoms, through a topological analysis of the electron density distribution, which is an observable and therefore it can be determined also experimentally.[13] A sufficient and necessary condition for a pair of atoms to be bonded is the existence of a bond path linking them,[11] implying the presence of a bond critical point (BCP) between the interconnected nuclei. However, although the BCP is an observable, the interpretation of the bond path in "chemical terms" may be not so immediate and the nature itself of a direct MM bond (if present) is not unambiguous.

In the first analyses reported in the literature, it was found that while molecules with unsupported MM bonds always feature a MM BCP, molecules with at least one bridging or semi-bridging carbonyl ligand lack of a MM BCP, with only few exceptions,[14] that are however controversial.[15] For example, although the 18-electron rule predicts a direct bond in the bridged isomer of $Co_2(CO)_8$, no BCP was found between the two cobalt atoms.[16] This automatically rules out a direct MM bond[12] and raises the question how to quantify the electron localization or delocalization in a bond. A generalization to other kinds of bridges is not so easy: Overgaard *et al.*[17–19] showed that the correct molecular graph may be difficult to ascertain in M_2C rings, especially from experimental electron densities.

On the other hand, even for unsupported MM bonds, the low values of electron density and Laplacian at the MM BCP produced somewhat ambiguous interpretation of the nature of this bond.[20] It became clear that a "traditional" QTAIM analysis, *i.e.* based only on the topology of the electron density distribution, was not sufficient to solve the dilemma and additional speculation was necessary. The more controversial case was the unsupported MM bond in $Mn_2(CO)_{10}$. Different hypotheses were proposed concerning the nature of the apparently direct MM bond. Both Bianchi[20] and Farrugia[21] measured experimentally the electron density ρ and analyzed the MM bond in terms of its Laplacian, $\nabla^2\rho$, typically used to classify bonds within QTAIM framework. Both studies found the BCP between the two metals and very similar values of ρ_{bcp} and $\nabla^2\rho_{\mathrm{bcp}}$. However, while Bianchi *et al.* classified the Mn-Mn interaction as *closed-shell* ("intermediate between ionic and covalent")[22] because of the positive $\nabla^2\rho_{\mathrm{bcp}}$, Farrugia used a more comprehensive analysis to conclude that the bond is instead covalent. Many other studies demonstrated that $\nabla^2\rho$ can be a misleading bond indicator in metal-organic chemistry,[23] because it is almost invariably positive, regardless the undisputed covalent nature of metal ligands interactions, especially cogent when magnetic super-exchange takes place.

In this respect, Gatti and Lasi,[24] analysing the source function,[25] demonstrated that most of the topological indexes fail to properly classify the MM bonds. This failure mainly concerns

the indices based on *one electron* properties, although the analysis of the energy density *H(r)* at the BCP could partially restore the connection between QTAIM and molecular orbital theory,[23] allowing to undoubtedly identify the typical features of covalent bonding (albeit weak). In the bridged isomer of $Co_2(CO)_8$, Finger *et al.*[26] found a *H(r)* minimum coinciding with the midpoint of the hypothetical CoCo bent-bond (of course, not associated with any bond path in the electron density). They concluded that an interaction between the two metals could be identified, even in the absence of a BCP. $Fe_2(CO)_9$ was even more controversial, especially because Reinhold *et al.*[27] found that the presence or absence of an FeFe BCP was dependent on the one electron basis used. By making a molecular orbital partition of the charge density, they could show that the bonding contribution is not totally overcome by the corresponding anti-bonding one, justifying the FeFe delocalization index[28] of 0.4 and claiming therefore a direct FeFe bond. On the other hand, still based on QTAIM arguments, Bauschlicher Jr. *et al.*[29] and Bo *et al.*[30] came to the opposite conclusion that no direct FeFe direct bond is present.

From this analysis of the literature, it is clear that the "traditional" QTAIM analysis of MM bonded systems lacks of unambiguous criteria to solve two major issues: a) the direct *vs.* indirect MM bond; b) the nature of the MM contribution to the bond. The limitations of analysing *just* the electron density are summarized by Farrugia and Macchi in a recent review: *"We can safely draw some conclusions, but some open problems remain and will probably continue do so - meaning that no direct link is probably possible between the concept of bond order and actual observable properties."*[6]

Trying to overcome the limitations of QTAIM, Ponec[31–34] investigated $M_2(CO)_n$ systems using Domain Averaged Fermi Hole (DAFH) analyses.[35–37] DAFH addresses a direct MM bond only for *unsupported* molecules, but M...CO interactions are also identified.[34] Multi-center bond is instead invoked for *supported* MM. This is a rephrasing of the original thesis proposed by Heijser *et al.*[38] The almost continuous bonding encompassing the transformation from unsupported to supported MM was first rationalized by Macchi *et al.*[28] using

delocalization indexes and anticipating the arguments later proposed by Ponec with DAFH analysis. However, one should consider that the nature of the electronic interaction in a system (two-center or multicenter, shared or closed-shell) does not necessarily inform us on its actual contribution to the molecular stability, which remains an open question to be discussed in the present work.

Given this scenario, it is evident that only a simultaneous breakdown of electron density *and* electronic energy could solve the remaining ambiguities for a comprehensive analysis of the metal-metal bond in carbonyl clusters. In this respect, the Interacting Quantum Atoms (IQA) approach,[39] an energy decomposition method based on the QTAIM real space partitioning, may be the ideal tool. IQA has been previously used to obtain chemically relevant information and to shed light on many aspects relative to chemical bonding and binding in a wide variety of systems,[40–46] including different metal-organic compounds.[47–49] The purpose of this article is to carry out similar IQA analyses on the MM interaction and bonding of the aforementioned dimetal polycarbonyl dimers.

The article is organized as it follows. First, we illustrate the basic concepts of the IQA approach and the computational details. Then, we will discuss on the MM interaction for bridged ($Co_2(CO)_8$), C_{2v} symmetry), unbridged ($Co_2(CO)_8$, $[Fe_2(CO)8]^{2-}$, D_{3d} symmetry) and semi-bridged ($[FeCo(CO)_8]^-$, C_s symmetry) systems, which are the prototypical examples of the bonding schemes used in most of the previous studies on this subject.[12,16,26,28,31–33,50–52] The analysis of these results will enable us to draw conclusions.

Theory and Computational Details

The IQA methodology has been fully described in earlier studies,[39,42,53–55] to which readers can refer for a more detailed explanation. Summarizing, within QTAIM the following one-

and two-basin partitioning of the molecular energy is used:

$$\begin{aligned} E &= \sum_A \int_{\Omega_A} d\boldsymbol{r}_1 \left[\hat{T} - \sum_B \frac{Z_B}{r_{1\mathrm{B}}} \right] \rho_1(\boldsymbol{r}_1; \boldsymbol{r}'_1) \\ &+ \frac{1}{2} \sum_{A,B} \int_{\Omega_A} d\boldsymbol{r}_1 \int_{\Omega_B} d\boldsymbol{r}_2 \frac{\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2)}{r_{12}} \\ &+ \sum_{A>B} \frac{Z_A Z_B}{R_{\mathrm{AB}}} \end{aligned} \tag{1}$$

where Ω_A represents the atomic basin of atom A, and $\rho_1(\boldsymbol{r}_1; \boldsymbol{r}'_1)$ and $\rho_2(\boldsymbol{r}_1; \boldsymbol{r}_2)$ are the first and second order reduced density matrices, respectively. The IQA approach joins now energetic terms such that chemically meaningful objects appear, in the light of McWeeny's theory of electronic separabilitiy.[56] Thus Eq. 1 becomes,

$$\begin{aligned} E &= \sum_A (T_A + V_{en}^{\mathrm{AA}} + V_{\mathrm{ee}}^{\mathrm{AA}}) \\ &+ \sum_{A>B} (V_{\mathrm{nn}}^{\mathrm{AB}} + V_{en}^{\mathrm{AB}} + V_{en}^{\mathrm{BA}} + V_{\mathrm{ee}}^{\mathrm{AB}}) \\ &= \sum_A E_{\mathrm{self}}^A + \sum_{A>B} E_{\mathrm{int}}^{\mathrm{AB}} \end{aligned} \tag{2}$$

in which A, B represent atoms; *i.e.* atomic basins plus their corresponding nuclei. Intra–basin contributions define an atomic self–energy, and all inter–basin ones the pairwise–additive interaction energy between pairs of atoms. Interactions are read in the chemical scale by decomposing ρ_2 into coulombic and exchange–correlation contributions,

$$\rho_2(\boldsymbol{r}_1; \boldsymbol{r}_2) = \rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2) - \rho_2^{\mathrm{xc}}(\boldsymbol{r}_1; \boldsymbol{r}_2) \tag{3}$$

($\rho(\boldsymbol{r}_1) = \rho_1(\boldsymbol{r}_1; \boldsymbol{r}_1)$). In equation (2), $V_{\mathrm{C}}^{\mathrm{AB}}$ is a purely coulombic term,

$$V_{\mathrm{C}}^{\mathrm{AB}} = \int_{\Omega_A} d\boldsymbol{r}_1 \int_{\Omega_B} d\boldsymbol{r}_2 \frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{r_{12}} \tag{4}$$

and $V_{\rm xc}^{\rm AB}$ is the exchange-correlation contribution to $V_{\rm ee}^{\rm AB}$,

$$V_{\rm xc}^{\rm AB} = -\int_{\Omega_A} d\boldsymbol{r}_1 \int_{\Omega_B} d\boldsymbol{r}_2 \frac{\rho_2^{\rm xc}(\boldsymbol{r}_1;\boldsymbol{r}_2)}{r_{12}} \tag{5}$$

In this way,

$$E_{\rm int}^{\rm AB} = V_{\rm cl}^{\rm AB} + V_{\rm xc}^{\rm AB} \tag{6}$$

where $V_{\rm cl}^{\rm AB}$ is the classical interaction energy,

$$V_{\rm cl}^{\rm AB} = (V_{\rm nn}^{\rm AB} + V_{en}^{\rm AB} + V_{en}^{\rm BA} + V_{\rm C}^{\rm AB}) \tag{7}$$

and $V_{\rm xc}^{\rm AB}$ is the purely quantum–mechanical exchange–correlation term, which contains the covalent interaction between atoms A and B. In fact, the delocalization index (DI) between atoms A and B, $\delta^{\rm AB}$, which is given by an expression very similar to Eq. 5,

$$\delta^{\rm AB} = 2\int_{\Omega_A} d\boldsymbol{r}_1 \int_{\Omega_B} d\boldsymbol{r}_2 \; \rho_2^{\rm xc}(\boldsymbol{r}_1;\boldsymbol{r}_2) \tag{8}$$

is a standard descriptor of the covalent bond order between both atoms in real space techniques.[57,58]

All the electronic structure calculations of this work were performed with the GAMESS code.[59] The molecular geometries of bridged, semi-bridged and unbridged molecules were optimized fixing their symmetries to C_{2v}, C_s, and D_{3d}, respectively (Figure 1). The standard 6-31G(d) basis-set (BS) was used for carbon and oxygen atoms whereas Hay-Wadt (HW) small ECPs with their respective BSs were chosen for transition metals.[60] The core density was reconstructed using a standard procedure, already described by some of us.[47]

All the calculations were performed at the DFT level of theory using the PBE functional.[61] Despite its popularity, some caution should be taken whenever a DFT method is used to calculate quantities which involve the 2nd order density matrix, like DIs or IQA analyses. Indeed the construction of such a matrix form the Kohn-Sham (KS) orbitals lacks

of a real theoretical justification. Hence, properties as δ^{AB} or V_{xc}^{AB} are approximated. Despite this, and probably due to the similarity between KS and HF wavefunctions, it has been found that the DFT values are comparable to the HF ones[62,63] and DFT provides a realistic description of the MM bond.[34,64,65] IQA analyses were performed with our PROMOLDEN code.

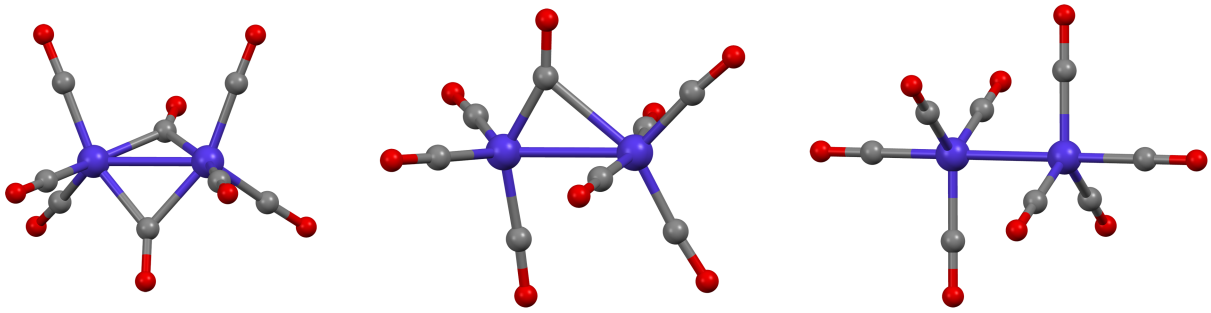

Figure 1: Left, the geometry of a bridged dimer $Co_2(CO)_8$ (C_{2v} symmetry); center, the geometry of a semi-bridged dimer, like $[FeCo(CO)_8]^-$ (C_s symmetry); right, the geometry of unbridged dimer, like $Co_2(CO)_8$ or $[Fe_2(CO)_8]^{2-}$ (D_{3d} symmetry) .

Results and Discussion

The unsupported dimers: $\mathbf{Co_2(CO)_8}$ and $\mathbf{[Fe_2(CO)_8]^{2-}}$

IQA results for the two unbridged molecules are summarized in Table 1. Despite $[Fe_2(CO)_8]^{2-}$ is di-anionic, the topological charges of the metals (Q_M) are very similar: 0.605 and 0.603 for Co and Fe respectively. On the contrary, the molecular charge strongly affects the MM distance, being 2.648 Å in the neutral Cobalt system and 2.847 Å in the di-anionic Iron dimer. As we will see, this elongation deeply affects the MM delocalization indexes and therefore the covalent contribution to the global interaction energy. Using a different basis set and DFT functionals, some of us reported in a previous paper[28] $\delta^{\mathrm{CoCo}} = 0.47$ for $Co_2(CO)_8$, comparable with $\delta^{\mathrm{CoCo}} = 0.42$ calculated in this work as described in the computational details. This delocalization is anyway smaller than expected for a 2c2e homopolar bond (*i.e.* 1.0). The residual electrons are shared between each metal and the equatorial carbonyls

bound to the other metal (*vicinal* carbonyls). In fact, the 1,3 M..CO interaction (Figure 2) gives a $\delta^{\mathrm{CoCO_{vicinal}}}$ of *ca* 0.1. Counting all the six 1,3 M...CO interactions and adding the CoCo sharing, we see that the total delocalization between the two moieties of the dimer corresponds to one electron pair. On the other hand, the MM lengthening in $[Fe_2(CO)_8]^{2-}$, causes a smaller delocalization between the two metals ($\delta^{\mathrm{FeFe}} = 0.314$), whereas $\delta^{\mathrm{FeCO_{vicinal}}}$ is similar to $\delta^{\mathrm{CoCO_{vicinal}}}$.

The results reported above explain the electron sharing process, but as discussed in the introduction we are interested in evaluating the actual sources of molecular stability. Thus, we analyze now the MM bond in terms of IQA. Since the metal atoms are positively charged, the electrostatic part of the MM interaction, $V_{\mathrm{cl}}^{\mathrm{MM}}$, is obviously destabilizing, and because the Co or Fe have similar charges, the amount of such destabilization (*ca* 0.06 au) is almost identical in the two compounds. The overall MM interaction energy, $E_{\mathrm{int}}^{\mathrm{MM}}$, is slightly stabilizing for the Co dimer but destabilizing for the Fe anion. This is due to the longer FeFe distance, which reduces the electron delocalization hence the covalent term, $V_{\mathrm{xc}}^{\mathrm{MM}}$. Noteworthy, V_{xc} is always stabilizing (*i.e.* negative), but in $[Fe_2(CO)_8]^{2-}$ the MM electron sharing is not large enough to compensate the coulombic repulsion giving a overall an unfavorable $E_{\mathrm{int}}^{\mathrm{MM}}$. Where does the stabilization comes from, then? The binding originates from the stabilizing interaction between the Fe atom of one $Fe(CO)_4$ moiety and the equatorial carbonyls of the other, namely $E_{\mathrm{int}}^{\mathrm{FeCO_{vicinal}}}$ = -0.043 au, see Table 1. This stabilization has itself two sources. One is the electrostatic interaction between the positively charged metal and the negatively charged oxygens, partly attenuated by the destabilization between the metal and the carbon atoms, both positively charged. The other source is the 1,3 M...CO electron sharing, in this case more favorable with the carbon (which is closer) but almost negligible with the oxygen. From Table 1, we learn that the electrostatic component is three times larger ($V_{\mathrm{cl}}^{\mathrm{MCO_{vicinal}}}$ = -0.033 au; $V_{\mathrm{xc}}^{\mathrm{MCO_{vicinal}}}$ = -0.011 au).

Table 1 shows that also for $Co_2(CO)_8$, the 1,3 Co..CO interactions play the dominant role

Table 1: DFT PBE metal-metal distance, QTAIM integrated properties, and IQA energetics profiles for the unbridged molecules. All data in atomic unit except distances in Angstrom.

M	$[Co_2(CO)_8]$	$[Fe_2(CO)_8]^{2-}$	M	$[Co_2(CO)_8]$	$[Fe_2(CO)_8]^{2-}$
d(MM)	2.648	2.847	Q_M	0.605	0.603
δ^{MM}	0.425	0.314	V_{cl}^{MM}	0.062	0.060
$\delta^{MCO_{vicinal}}$	0.101	0.107	$V_{cl}^{MCO_{vicinal}}$	−0.014	−0.033
$\delta^{MC_{vicinal}}$	0.075	0.078	$V_{cl}^{MC_{vicinal}}$	0.078	0.064
$\delta^{MO_{vicinal}}$	0.026	0.029	$V_{cl}^{MO_{vicinal}}$	−0.092	−0.097
E_{int}^{MM}	−0.006	0.060	V_{xc}^{MM}	−0.068	−0.048
$E_{int}^{MCO_{vicinal}}$	−0.028	−0.043	$V_{xc}^{MCO_{vicinal}}$	−0.014	−0.013
$E_{int}^{MC_{vicinal}}$	0.066	0.053	$V_{xc}^{MC_{vicinal}}$	−0.012	−0.011
$E_{int}^{MO_{vicinal}}$	−0.094	−0.100	$V_{xc}^{MO_{vicinal}}$	−0.002	−0.002

in assembling the two moieties to form the molecule. In fact, the direct interaction between the two metals (sum of covalent and electrostatic contributions), although stabilizing, is smaller compared to the 1,3 Co...CO interactions. This observation is in keeping with what was originally proposed by Brown *et al.*[66] who computed with semi-empirical methods a large stabilization in $Mn_2(CO)_{10}$ due to the 1,3 Mn...CO electrostatic interactions. The 1,3 M...CO interactions are stronger in the anion, because the π-acidic carbonyls localize the electrons in excess, making C atoms less positively charged and O atoms more negative. As a result, $V_{cl}^{MCO_{vicinal}}$ is more stabilizing in the anion, despite the slightly longer M...O distances. This favourable interaction is however compensated by a destabilization produced by the interactions amongst the equatorial carbonyls of the two moieties, giving $E_{int}^{CO_{eq}CO_{eq}} = 0.031$ au. On the contrary, in the neutral $Co_2(CO)_8$ the CO....CO interaction is slightly stabilizing $E_{int}^{CO_{eq}CO_{eq}}$ = -0.015 au). In both dimers the electrostatic contribution to this interaction is destabilizing, $V_{cl}^{CO_{eq}CO_{eq}}$ is 0.010 au in $Co_2(CO)_8$ and 0.058 au in $[Fe_2(CO)_8]^{2-}$. Nevertheless, minor electron sharing is calculated amongst the equatorial carbonyls ($\delta_{Co_2(CO)8}^{CO_{eq}CO_{eq}} = 0.008$ and $\delta_{[Fe_2(CO)_8]^{2-}}^{CO_{eq}CO_{eq}} = 0.007$, see the Supporting Information for more details) yielding a small covalent contribution of $V_{xc}^{CO_{eq}CO_{eq}}$ = -0.025 au and -0.027 au for $Co_2(CO)_8$ and $[Fe_2(CO)_8]^{2-}$, respectively. As discussed in our previous work on classical and non-classical metal carbonyl complexes,[63] the electron delocalization in the M-CO bonds is quite large, *e.g.* $\delta^{FeCO_{ax}} =$

1.3, and therefore the interaction energy is largely stabilizing, $E_{\rm int}^{\rm FeCO_{ax}}$ = -0.26 au ($V_{\rm cl}^{\rm FeCO_{ax}}$ = 0.01 au; $V_{\rm xc}^{\rm FeCO_{ax}}$ = -0.27 au). We will not further discuss these interactions here, given that the subject is actually the interaction between two metal moieties.

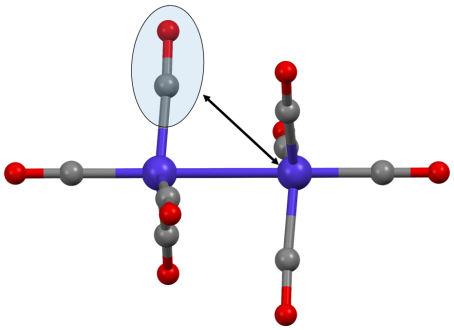

Figure 2: 1,3 M..CO interaction between M and one of the $CO_{\rm vicinal}$ in unsupported dimers. This long interaction, characterized by a $\delta^{\rm MCO_{vicinal}}$ *ca* 0.1 and an $E_{\rm int}^{\rm MCO_{vicinal}}$ *ca* −0.150 au, has been found to be the main factor responsible for monomer binding.

The symmetrical bridge: $Co_2(CO)_8$

The more relevant IQA results for this molecule are collected in Table 2. As anticipated in the introduction, bridged metal dimers do not show any direct MM bond path. Therefore, the C_{2v} isomer of $Co_2(CO)_8$ is perfectly representative of this class of compounds. The molecular graph features two M-C bond paths for each bridging carbonyl, $CO_{\rm bridge}$. The bridge implies a shorter distance between the two moieties ($d_{\rm CoCo}$ = 2.546 Å) compared to the unbridged case ($d_{\rm CoCo}$ = 2.648 Å). Despite the shorter contact, the delocalization index between the two metals is smaller ($\delta^{\rm CoCo}$ =0.33), because the two $C_{\rm bridge}$ atomic basins protrude into the space region of the CoCo interaction. As commented in the introduction, it is now quite accepted that a delocalized multicenter bond takes place amongst cobalts and the bridging carbonyls. Summing $\delta^{\rm CoCo}$ with $\delta^{\rm CoCO_{bridge}}$ gives *ca* 2.0 electron pairs shared inside the bridge system, which confirms the 3c2e nature of each bridge interaction.

It is again interesting to analyse the electron density distribution under the special perspective offered by IQA. The CoCo interaction is now associated with a destabilization,

because the weaker electron sharing is not able to compensate the increased electrostatic repulsion (0.009 au) between same charge atoms. Although Q_M is slightly smaller than in the unbridged dimer, the MM distance is now shorter and therefore the coulombic destabilization is larger. Given the smaller δ^{CoCo}, V_{xc}^{CoCo} is also smaller than in unsupported MM dimers. Interestingly, V_{xc}^{CoCo} is very similar to that calculated for $[Fe_2(CO)_8]^{2-}$, where it is the longer MM distance that quenches the electron sharing. On the other hand, the $CoCO_{bridge}$ interactions are obviously weaker than the terminal Co-CO ones, given that the bridging carbon is now sharing electrons with two metals and that the CoC_{bridge} distance is longer.

While for the unsupported dimers the molecular graph cannot provide a comprehensive picture of the electron delocalization mechanism, for bridged dimers the IQA scenario coincides with the *through bond* interaction identified by the QTAIM analysis of the electron density distribution, from theory as well as from experiment.[67] In fact, the presence of MC_{bridge} bond paths, inwardly curved in the M-C-M ring was recognized as a clear sign of multi-center bonding. Moreover, this view is in agreement with the DAFH picture, later proposed by Ponec *et al.*[32,34]

The analysis of the individual $E_{int}^{CoCO_{bridge}}$ contributions reveals a quite large covalent term ($V_{xc}^{MC_{bridge}}$ = -0.161 au) and two strong coulombic interactions, though of opposite sign ($V_{cl}^{MC_{bridge}}$ = 0.094 au and $V_{cl}^{MO_{bridge}}$ = -0.121 au). Overall, this means that the stabilization comes in part from the interaction between Co and C ($E_{int}^{CoCO_{bridge}}$ = -0.670 au), in which the covalent term is dominating, and in part from the interaction between Co and O ($V_{int}^{MO_{bridge}}$ = -0.136 au), in which the electrostatic part is overwhelming. Clearly, the observed molecular graph is able to reveal only the former, because produced by electron sharing and therefore with direct implications for the electron distribution, but not the latter, which is actually more effective.

Table 2: DFT PBE distances, QTAIM integrated properties, and IQA energetics profiles for bridged and semi-bridged molecules. All data in atomic unit except distances in Angstrom.

M	$[Co_2(CO)_8]$	$[FeCo(CO)_8]^-$	M	$[Co_2(CO)_8]$	$[FeCo(CO)_8]^-$
d(MM)	2.546	2.626	Q_{Co}	0.551	0.554
$d(CoC_{bridge})$	1.954	1.832	Q_{Fe}		0.667
$d(FeC_{bridge})$		2.193			
δ^{MM}	0.328	0.294	V_{cl}^{MM}	0.071	0.075
$\delta^{CoCO_{bridge}}$	0.824	1.008	$V_{cl}^{CoCO_{bridge}}$	−0.027	−0.032
$\delta^{CoC_{bridge}}$	0.676	0.897	$V_{cl}^{CoC_{bridge}}$	0.094	0.101
$\delta^{CoO_{bridge}}$	0.148	0.183	$V_{cl}^{CoO_{bridge}}$	−0.121	−0.133
$\delta^{FeCO_{bridge}}$		0.543	$V_{cl}^{FeCO_{bridge}}$		−0.055
$\delta^{FeC_{bridge}}$		0.442	$V_{cl}^{FeC_{bridge}}$		0.091
$\delta^{FeO_{bridge}}$		0.101	$V_{cl}^{FeO_{bridge}}$		−0.146
E_{int}^{MM}	0.025	0.030	V_{xc}^{MM}	−0.047	−0.045
$E_{int}^{CoCO_{bridge}}$	−0.203	−0.267	$V_{xc}^{MCO_{bridge}}$	−0.176	−0.236
$E_{int}^{CoC_{bridge}}$	−0.067	−0.117	$V_{xc}^{CoC_{bridge}}$	−0.161	−0.218
$E_{int}^{CoO_{bridge}}$	−0.136	−0.150	$V_{xc}^{CoO_{bridge}}$	−0.015	−0.018
$E_{int}^{FeCO_{bridge}}$		−0.162	$V_{xc}^{FeCO_{bridge}}$		−0.108
$E_{int}^{FeC_{bridge}}$		−0.006	$V_{xc}^{FeC_{bridge}}$		−0.098
$E_{int}^{FeO_{bridge}}$		−0.156	$V_{xc}^{FeO_{bridge}}$		−0.010

The semi-bridged molecule: $[FeCo(CO)_8]^-$

The more relevant IQA results for this molecule are collected in Table 2. $[FeCo(CO)_8]^-$ is isoelectronic with $[Co_2(CO)_8]$, but it is known only in one isomer, the very peculiar "semi-bridging" stereochemistry. Only one carbonyl approaches a bridging position, but remaining closer to Co ($d_{CoC_{bridge}}$ = 1.832 Å, $d_{FeC_{bridge}}$ = 2.193 Å). As already reported, the molecular graph of this compound is topologically equivalent to that of a symmetrical bridge, having two MC_{bridge} bond paths but no MM one.[28] As in the other compounds, the metals are positively charged, (Q_{Co} = 0.554; Q_{Fe} = 0.667). Because of the negative charge and the absence of a strong bridge, FeCo distance (d_{FeCo} = 2.626 Å) is longer than in the bridged isomer of $Co_2(CO)_8$ but shorter than the unbridged and double-charged $[Fe_2(CO)_8]^{2-}$. The delocalization indexes reflect the geometrical features: δ^{CoFe} = 0.29, similar to the anionic unsupported bond or the neutral bridged bond; $\delta^{CoCO_{bridge}}$ = 1.00, similar to a normal terminal carbonyl[63] and definitely larger that the interaction in the symmetric bridge described

above; $\delta^{\mathrm{FeCO_{bridge}}} = 0.54$, smaller than that of the symmetric bridge.

Again the IQA analysis enables the association of the electron density distribution with the energy breakdown. While the MM interaction is extremely similar to that in the $Co_2(CO)_8$ bridged isomer, more interesting is the analysis of the interaction between the metals and C_{bridge}. The shorter bond, $CoCO_{bridge}$, features a strong quantum mechanical stabilization ($V_{xc}^{\mathrm{CoC_{bridge}}}$ = -0.218 au), partially attenuated by the electrostatic repulsion between two identically charged atoms ($V_{cl}^{\mathrm{CoC_{bridge}}} = 0.101$ au), yielding a final $CoCO_{bridge}$ interaction energy of -0.117 au, comparable to that of terminal carbonyls.[63] The Co-O term also conforms. For the $FeCO_{bridge}$ interaction, the total interaction energy ($E_{int}^{\mathrm{FeCO_{bridge}}}$ = -0.162 au), contains three almost equally strong components: the stabilizing FeC_{bridge} electron sharing, the destabilizing FeC_{bridge} electrostatic interaction and the stabilizing FeO_{bridge}, see Table 2. It is interesting that just a minor perturbation of the terminal carbonyl produces a stronger stabilization of the 1,3 M—CO interaction. Consequently, the semi-bridging appears as the sum of an almost pure $MC_{terminal}$ and an almost pure MC_{bridge} interactions. From Tables 1 and 2, one can estimate the stability provided by the various types of carbonyls to the dimer. The ranking would be $CO_{semi-bridging} > CO_{bridging} > CO_{terminal}$. However, one should also consider that the presence of bridging or semi-bridging carbonyls significantly modifies the stereochemistry at the metal centers and the 1,3 M...Co interactions are quite inhibited. Therefore, although less stabilizing, terminal carbonyls enable to maximize the number of 1,3 M...CO and therefore they guarantee a stability similar of that of bridging groups.

Conclusions

In this paper, we have adopted for the first time the IQA method to investigate the full conformational space of metal carbonyl dimers, showing that this approach is able to complement the information normally available from traditional QTAIM analysis of the electron density distribution, and even from analysis of the pair distribution. The simple molecular

graph and the study of local properties of the electron density may not suffice to describe the complexity of multicenter bonding, like that occurring in transition metal dimers. Even if information on the electron delocalization is available, as from delocalization indexes or DAFH, the relative importance of electron sharing and electrostatic interactions is not available. This is why IQA offers the more comprehensive view and helps sorting out ambiguities.

We can safely conclude that a delocalized multicenter MM bond is always present in $[M_2(CO)_8]^n$ systems, involving the two metals and all the carbonyls insisting on the MM connection (either terminal, semi-bridging or bridging). Of course, the interplay between the MM and M-CO bonding configurations depends on the actual molecular geometry, but the mechanism is basically the same, in keeping with previous formulations by Macchi *et al.*[28] and by Ponec and Gatti.[33] This scheme is now corroborated not only by the calculated electron sharing between the two metals (always smaller than one electron pair), but also by the total MM interaction energies. The IQA analysis shows that there is always a strong MM covalent component, which is normally opposed by an electrostatic repulsion. In fact, despite being formally "zerovalent", the metals in carbonyl complexes always bear a positive charge (*ca.* 0.5). The other covalent component arises of course from the electron sharing between M and the carbonyl C, which decreases on going from terminal to bridging and eventually to vicinal carbonyl. Nevertheless, this component is always present, even for the 1,3 M...CO interactions, but of course its weight decreases along this series. There are two electrostatic components in the M-CO interaction: one is always repulsive (M-C), the other is always attractive (M-O). The M...O electrostatic attraction is the most important to explain the stability of bridges and semi-bridges as well as to explain the relevant role of 1,3 M...CO in gluing the two metal moieties in so-called "unsupported" metal-metal bond, in keeping with the old hypothesis suggested by Brown.*et al.*,[66] although based on highly approximated semi-empirical calculations. In view of this latter observation, the term "unsupported" appears inappropriate.

Some questions remain open, concerning the backdonation from M to CO_{bridge}, in par-

ticular its role in the semi-bridging complex. It is generally supposed supposed that bridged carbonyls are more π-acidic than terminal ones and that therefore a direct MM bond can be formed only when no π acceptor ligand insist on the MM connection. We have recently proposed a method that, combining IQA and DAFH approaches, is able to recover the molecular orbital language from a real space descriptions.[68] However, the computational efforts for a full IQA-DAFH analysis is, at the moment, too expensive. A future parallelization of PROMOLDEN code will allow to increase the size of the systems suitable to be studied with this new approach.

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References

(1) Powell, H. M.; Ewens, R. V. G. 64. The Crystal Structure of Iron Enneacarbonyl. *J. Chem. Soc.* **1939**, 286–292.

(2) Dahl, L.; Ishishi, E.; Rundle, R. E. Polynuclear Metal Carbonyls. I. Structures of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. *J. Chem. Phys.* **1957**, *26*, 1750–1751.

(3) Dahl, L. F.; Rundle, R. E. The Crystal Structure of Dimanganese Decacarbonyl $Mn_2(CO)_{10}$. *Acta Cryst.* **1963**, *16*, 419–426.

(4) Sumner, G. G.; Klug, H. P.; Alexander, L. E. The Crystal Structure of Dicobalt Octacarbonyl. *Acta Cryst.* **1964**, *17*, 732–742.

(5) Summerville, R. H.; Hoffmann, R. M_2L_9 complexes. *J. Am. Chem. Soc.* **1979**, *101*, 3821–3831.

(6) Farrugia, L.; Macchi, P. *Electron Density and Chemical Bonding I*; Structure and Bonding; Springer Berlin Heidelberg, 2012; Vol. 146; pp 127–158.

(7) Reinhold, J.; Kluge, O.; Mealli, C. Integration of Electron Density and Molecular Orbital Techniques to reveal Questionable Bonds: The Test Case of the Direct Fe-Fe Bond in $Fe_2(CO)_9$. *Inorg. Chem.* **2007**, *20*, 7142–7147.

(8) Martin, M.; Rees, B.; Mitschler, A. Bonding in a Binuclear Metal Carbonyl: Experimental Charge Density in $Mn_2(CO)_{10}$. *Acta Cryst.* **1982**, *B38*, 6–15.

(9) Coppens, P.; Hall, M. *Electron Distribution and the Chemical Bond*; Plenum Press: NY, 1982.

(10) Brown, D.; Chambers, W.; Fitzpatrick, N.; Rawilson, R. Molecular Orbital Theory of Organometallic Compounds. Part XII. Nature of Metal-Metal Bonding in Some Binuclear Metal Carbonyls. *J. Chem. Soc. A* **1971**, 720–725.

(11) Bader, R. F. W. A Bond Path: A Universal Indicator of Bonded Interactions. *J. Phys. Chem. A* **1998**, *102*, 7314–7323.

(12) Low, A. A.; Kunze, K. L.; MacDougall, P. J.; Hall, M. B. Nature of Metal-Metal Interactions in Systems with Bridging Ligands. 1. Electronic Structure and Bonding in Octacarbonyldicobalt. *Inorg. Chem.* **1991**, *30*, 1079–1086.

(13) Coppens, P. *X-ray charge density and chemical bonding*; Oxford Science Publications: Oxford, 1997.

(14) Bianchi, R.; Gervasio, G.; Marabello, D. Experimental Electron Density in the Triclinic Phase of $Co_2(CO)_6$(l-CO)(l-$C_4H_2O_2$)) at 120 K. *Acta Cryst.* **2001**, *B57*, 638–645.

(15) Farrugia, L. Is there a Co-Co Bond Path in $Co_2(CO)_6$(l-CO)(l-$C_4H_2O_2$)? *Chem. Phys. Lett.* **2005**, *414*, 122–126.

(16) Macchi, P.; Sironi, A. Chemical Bonding in Transition Metal Carbonyl Clusters: Complementary Analysis of Theoretical and Experimental Electron Densities. *Coord. Chem. Rev.* **2003**, *238-239*, 383–412.

(17) Platts, J.; Evans, G.; Coogan, M.; Overgaard, J. Electronic Structure of the Alkyne-Bridged Dicobalt Hexacarbonyl Complex Co_2(l-$C_2H_2$$(CO)_6$: Evidence for Singlet Diradical Character and Implications for Metal-Metal Bonding. *Inorg. Chem.* **2007**, *46*, 6291–6298, cited By (since 1996)16.

(18) Overgaard, J.; Clausen, H.; Platts, J.; Iversen, B. Experimental and theoretical Charge Density Study of Chemical Bonding in a Co Dimer Complex. *J. Am. Chem. Soc.* **2008**, *130*, 3834–3843.

(19) Overgaard, J.; Platts, J.; Iversen, B. Experimental and Theoretical Charge-Density Study of a Tetranuclear Cobalt Carbonyl Complex. *Acta Cryst.* **2009**, *B65*, 715âĂŞ723.

(20) Bianchi, R.; Gervasio, G.; Marabello, D. Experimental Electron Density Analysis of $Mn_2(CO)_{10}$: Metal-Metal and Metal-Ligand Bond Characterization. *Inorg. Chem.* **2000**, *39*, 2360–2366.

(21) Farrugia, L. J.; Mallinson, P. R.; Stewart, B. Experimental Charge Density in the Transition Metal Complex $Mn_2(CO)_{10}$: a Comparative Study. *Acta Cryst.* **2003**, *B59*, 234–247.

(22) Bianchi, R.; Gervasio, G.; Marabello, D. Experimental charge Density Study of the MnâĂŞMn Bond in $Mn_2(CO)_10$ at 120 K. *Chem. Comm.* **1998**, 1535–1536.

(23) Macchi, P.; Proserpio, D. M.; Sironi, A. Experimental Electron Density in a Transition Metal Dimer: Metal-Metal and Metal-Ligand Bonds. *J. Am. Chem. Soc.* **1998**, *120*, 13429–13435.

(24) Gatti, C.; Lasi, D. Source Function Description of Metal-Metal Bonding in d-Block Organometallic Compounds. *Faraday Discuss.* **2007**, *135*, 55–78.

(25) Bader, R. F.; Gatti, C. A Green's Function for the Density. *Chem. Phys. Lett.* **1998**, *287*, 233 – 238.

(26) Finger, M.; Reinhold, J. Energy Density Distribution in Bridged Cobalt Complexes. *Inorg. Chem.* **2003**, *42*, 8128–8130.

(27) Reinhold, J.; Kluge, O.; Mealli, C. Integration of Electron Density and Molecular Orbital Techniques to Reveal Questionable Bonds: The Test Case of the Direct FeâĹŠFe Bond in $Fe_2(CO)_9$. *Inorg. Chem.* **2007**, *46*, 7142–7147.

(28) Macchi, P.; Garlaschelli, L.; Sironi, A. Electron Density of Semi-Bridging Carbonyls. Metamorphosis of CO Ligands Observed via Experimental and Theoretical Investigations on [FeCo(CO)8]-. *J. Am. Chem. Soc.* **2002**, *124*, 14173–14184.

(29) Bauschlicher, C. W. On the Bonding in $Fe_2(CO)_9$. *J. Chem. Phys.* **1986**, *84*, 872–975.

(30) Bo, C.; Sarasa, J. P.; Poblet, J. M. Laplacian of Charge Density for Binuclear Complexes: Terminal vs Bridging Carbonyls. *J. Phys. Chem.* **1993**, *97*, 6362–6366.

(31) Ponec, R.; Lendvay, G.; Chaves, J. Structure and Bonding in Binuclear Metal Carbonyls from the Analysis of Domain Averaged Fermi Holes. I. $Fe_2(CO)_9$ and $Co_2(CO)_8$. *J. Computat. Chem.* **2008**, *29*, 1387–1398.

(32) Ponec, R.; Lendvay, G.; Sundberg, M. R. Structure and Bonding in Binuclear Metal Carbonyls from the Analysis of Domain Averaged Fermi Holes. 2. ${Fe_2(CO)_8}^{2-}$ and $Fe_2(CO)_8$. *J. Phys. Chem. A* **2008**, *112*, 9936–9945.

(33) Ponec, R.; Gatti, C. Do the Structural Changes Defined by the Electron Density Topology Necessarily Affect the Picture of the Bonding? *Inorg. Chem.* **2009**, *48*, 11024–11031.

(34) Ponec, R.; Yuzhakov, G.; Sundberg, M. R. Chemical Structures from the Analysis of Domain-Averaged Fermi Holes. Nature of the Mn-Mn Bond in Bis(pentacarbonylmanganese). *J. Comput. Chem.* **2005**, *26*, 447–454.

(35) Ponec, R. Electron Pairing and Chemical Bonds. Chemical Structure, Valences and Structural Similarities from the Analysis of the Fermi Holes. *J. Math. Chem.* **1997**, *21*, 323–333.

(36) Ponec, R. Electron Pairing and Chemical Bonds. Molecular Structure from the Analysis of Pair Densities and Related Quantities. *J. Math. Chem.* **1998**, *23*, 85–103.

(37) Ponec, R.; Duben, A. J. Electron Pairing and Chemical Bonds: Bonding in Hypervalent Molecules from Analysis of Fermi Holes. *J. Comp. Chem.* **1999**, *20*, 760–771.

(38) Heijser, W.; Baerends, E. J.; Ros, P. Electronic Structure of Binuclear Metal Carbonyl Complexes. *Faraday Symp. Chem. Soc.* **1980**, *14*, 211–234.

(39) Blanco, M. A.; Mart'in Pendás, A.; Francisco, E. Interacting Quantum Atoms: A Correlated Energy Decomposition Scheme Based on the Quantum Theory of Atoms in Molecules. *J. Chem. Theor. Comput.* **2005**, *1*, 1096–1109.

(40) Pendás, A. M.; Francisco, E.; Blanco, M. A. Binding Energies of First Row Diatomics in the Light of the Interacting Quantum Atoms Approach. *J. Phys. Chem. A* **2006**, *110*, 12864–12869.

(41) Martín Pendás, A.; Blanco, M. A.; Francisco, E. The Nature of the Hydrogen Bond: a Synthesis from the Interacting Quantum Atoms Picture. *J. Chem. Phys.* **2006**, *125*, 184112–184120.

(42) Pendás, A. M.; Blanco, M. A.; Francisco, E. Chemical Fragments in Real Space: Definitions, Properties, and Energetic Decompositions. *J. Comput. Chem.* **2007**, *28*, 161–184.

(43) Martín Pendás, A.; Francisco, E.; Blanco, M. A. Charge Transfer, Chemical Potentials, and the Nature of Functional Groups: Answers from Quantum Chemical Topology. *Faraday Discuss.* **2007**, *135*, 423–438.

(44) Pendás, A. M.; Francisco, E.; Blanco, M. A.; Gatti, C. Bond Paths as Privileged Exchange Channels. *Chemistry, Eur. J.* **2007**, *13*, 9362–9371.

(45) Pendás, A. M.; Blanco, M. A.; Francisco, E. Steric Repulsions, Rotation Barriers, and Stereoelectronic Effects: A Real Space Perspective. *J. Comput. Chem.* **2009**, *30*, 98–109.

(46) García-Revilla, M.; Popelier, P. L. A.; Francisco, E.; Martín Pendás, A. Nature of Chemical Interactions from the Profiles of Electron Delocalization Indices. *J. Chem. Theor. Comput.* **2011**, *7*, 1704–1711.

(47) Tiana, D.; Francisco, E.; Blanco, M. A.; Pendás, A. M. Using Pseudopotentials within the Interacting Quantum Atoms Approach. *J. Phys. Chem. A* **2009**, *113*, 7963–7971.

(48) Tiana, D.; Francisco, E.; Blanco, M. A.; Macchi, P.; Sironi, A.; Martín Pendás, A. Bonding in Classical and Nonclassical Transition Metal Carbonyls: The Interacting Quantum Atoms Perspective. *J. Chem. Theor. Comput.* **2010**, *6*, 1064–1074.

(49) Tiana, D.; Francisco, E.; Blanco, M. A.; Macchi, P.; Sironi, A.; Pendás, A. M. Restoring Orbital Thinking from Real Space Descriptions: Bonding in Classical and Non-Classical Transition Metal Carbonyls. *Phys. Chem. Chem. Phys.* **2011**, *13*, 5068–5077.

(50) Freund, H.-J.; Hohlneicher, G. Calculation of Transition Metal Compounds Using an Extension of the CNDO Formalism. *Theoret. Chim. acta* **1979**, *51*, 145–162.

(51) Freund, H.-J.; Dick, B.; Hohlneicher, G. Calculation of Transition Metal Compounds Using an Extension of the CNDO Formalism. *Theoret. Chim. acta* **1980**, *57*, 181–207.

(52) Leung, P. C.; Coppens, P. Experimental Charge Density Study of Dicobalt Octacarbonyl and Comparison with Theory. *Acta Cryst.* **1983**, *B39*, 535–542.

(53) Pendás, A. M.; Blanco, M. A.; Francisco, E. Two-electron Integrations in the Quantum Theory of Atoms in Molecules. *J. Chem. Phys.* **2004**, *120*, 4581–4592.

(54) Pendás, A. M.; Francisco, E.; Blanco, M. A. Two-electron Integrations in the Quantum Theory of Atoms in Molecules with Correlated Wave Functions. *J. Comput. Chem.* **2005**, *26*, 344–351.

(55) Francisco, E.; Martín Pendás, A.; Blanco, M. A. A Molecular Energy Decomposition Scheme for Atoms in Molecules. *J. Chem. Theor. Comput.* **2006**, *2*, 90–102.

(56) McWeeny, R. *Methods of Molecular Quantum Mechanics*, 2nd ed.; Academic Press: London, 1992; Chapter 14.

(57) Angyan, J. G.; Loos, M.; Mayer, I. Covalent Bond Orders and Atomic Valence Indices in the Topological Theory of Atoms in Molecules. *J. Phys. Chem.* **1994**, *98*, 5244–5248.

(58) Fradera, X.; Austen, M. A.; Bader, R. F. W. The Lewis Model and Beyond. *J. Phys. Chem. A* **1999**, *103*, 304–314.

(59) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. et al. General atomic and molecular electronic structure system. *J. Comput. Chem.* **1993**, *14*, 1347–1363.

(60) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *J. Chem. Phys.* **1985**, *82*, 299–310.

(61) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(62) Wang, Y.-G.; Matta, C.; Werstiuk, N. H. Comparison of Localization and Delocalization Indices Obtained with Hartree Fock and Conventional Correlated Methods: Effect of Coulomb Correlation. *J. Comput. Chem.* **2003**, *24*, 1720–1729.

(63) Tiana, D.; Francisco, E.; Blanco, M. A.; Macchi, P.; Sironi, A.; Martín Pendás, A. Bonding in Classical and Nonclassical Transition Metal Carbonyls: The Interacting Quantum Atoms Perspective. *J. Chem. Theor. Comput.* **2010**, *6*, 1064–1074.

(64) Ponec, R.; Yuzhakov, G.; Carbo-Dorca, R. Chemical Structures from the Analysis of Domain-Averaged Fermi Holes: Multiple Metal-Metal Bonding in Transition Metal Compounds. *J. Comput. Chem.* **2003**, *24*, 1829–1838.

(65) Ponec, R.; Feixas, F. Peculiarities of Multiple CrâĹŠCr Bonding. Insights from the Analysis of Domain-Averaged Fermi Holes. *J. Phys. Chem. A* **2009**, *113*, 8394–8400.

(66) Brown, D. A.; Chambers, W. J.; Fitzpatrick, N. J.; Rawlinson, R. M. Molecular Orbital Theory of Organometallic Compounds. Part XII. Nature of Metal-Metal Bonding in Some Binuclear Metal Carbonyls. *J. Chem. Soc. A* **1971**, 720–725.

(67) Macchi, P.; Garlaschelli, L.; Martinengo, S.; Sironi, A. Charge Density in Transition Metal Clusters: Supported vs. Unsupported Metal-Metal Interactions. *J. Am. Chem. Soc.* **1999**, *121*, 10428–10429.

(68) Tiana, D.; Francisco, E.; Blanco, M. A.; Macchi, P.; Sironi, A.; Pendás, A. M. Restoring Orbital Thinking from Real Space Descriptions: Bonding in Classical and Non-Classical Transition Metal Carbonyls. *Phys. Chem. Chem. Phys.* **2011**, *13*, 5068–5077.

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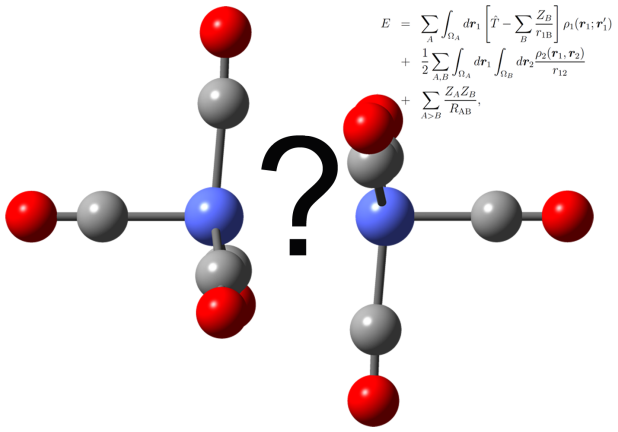

TOC

The Interacting Quantum Atom approach allows to quantify the bonding contributions in transition metal carbonyl dimers, solving long standing questions about the source of stability in these molecules